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## PATENT SPECIFICATION

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## (54) SEMI-PERMEABLE COMPOSITE MEMBRANES

- (71) We, **RHONE-POULENC INDUSTRIES**, a French Body Corporate, of 22 Avenue Montaigne, 75360 Paris Cedex 08, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to membranes.
- The composite membranes, according to the present invention, which can be used especially in reverse osmosis and hyperfiltration, are characterised in that they comprise, applied to one another,
- a) an external skin consisting of a polymer which is water-insoluble, is active in reverse osmosis and has a sufficiently high molecular weight for the anisotropic ultrafiltration membrane b) to exhibit a degree of rejection of 100% with respect to solutions of this polymer, and
- b) an anisotropic ultrafiltration membrane of an acrylonitrile polymer, the external skin a) being in contact with at least the less porous side of the anisotropic ultrafiltration membrane b).
- For convenience of terminology, the description "membrane" is used herein for layer b) of the composite membrane though, of course, one is not dealing with an isolated membrane but only with one constituent of the composite membrane.
- The composite membranes of this invention for reverse osmosis are generally ones wherein the external skin a) has a total thickness not exceeding  $3\mu$ , preferably not exceeding  $1\mu$ .
- In practice, the external skin a) and the anisotropic ultrafiltration membrane b) adhere to one another. The anisotropic ultrafiltration membrane b) possesses a so-called intermediate skin. The external skin a) of the composite membrane is in contact with this intermediate skin which constitutes the less porous side of the anisotropic ultrafiltration membrane b).
- By the term "polymer which is active in reverse osmosis", as used herein, is meant a polymer which, when converted to an ordinary dense film and used in a reverse osmosis operation on a saline solution, exhibits a degree of rejection of salt which is not zero and is, in particular, at least 30%.
- In the composite membranes for reverse osmosis, the external skin a) can either be dense throughout or partially dense, that is to say comprise a dense layer (i.e. non-porous layer—see below) and a porous layer. In the composite hyperfiltration membranes, the external skin a) exhibits a degree of porosity throughout, this porosity need not be uniform from one face of the skin a) to the other.
- External Skin a)
- As the external skin, any natural, artificial or synthetic polymer which is water-insoluble and is active in reverse osmosis may be used.
- Of course, the polymers concerned must have a sufficiently high molecular weight to be film-forming. Furthermore, the molecular weight distribution should be such that there is virtually no low molecular weight material which could permeate through the anisotropic ultrafiltration membrane b) in an ultrafiltration operation.
- Suitable polymers which can constitute the external skin a) in the reverse osmosis and hyperfiltration membranes include cellulose ethers and cellulose esters, especially cellulose

acetates, such as diacetates and triacetates and acetates having an intermediate degree of acetylation. However, it is preferred to use, as the polymer constituting the external skin, a polymer having sulphonic acid groups or a polymer having quaternary ammonium groups, the polymers being insoluble in water, such as those which can be used for the manufacture of the anisotropic ultrafiltration membrane b) of Application No. 52270/74 (Serial No. 1,473,857), to which reference should be made for further details. Amongst these polymers, there may be mentioned especially the (optionally salified) sulphonated polyarylether-sulphones, such as those described in U.S. Patent No. 3,709,841.

As already stated, the external skin a) can be dense, porous or partially porous.

The term "dense" film or "dense" as used herein, means a polymer structure which is substantially free from pores and micropores, especially from micropores of diameter greater than 10Å. If the external skin a) is partially porous, the porosity can be distributed uniformly through the thickness of the skin, but it is also possible for the external skin a) itself to have an anisotropic structure, that is to say a porous part and one or two dense surface layers. It is thus possible to define a porosity  $P_y$  of the external skin such that

$$P_y = 100 \left( 1 - \frac{et}{mt} \right),$$

wherein  $mt$  = measured thickness of the external skin (measured on sections under an electron microscope) and  $et$  = the equivalent thickness of this same external skin;  $et$  is calculated by measuring the permeability of the composite membrane and comparing this permeability with that of a dense film consisting of the same polymer as the external skin (such a dense film can be obtained by casting a polymer solution and evaporating the solvent). In general, in the present invention,  $P_y$  is less than 90% for reverse osmosis membranes, frequently from 1 to 60%.

For composite hyperfiltration membranes, the external skin a) is sufficiently porous for the degree of rejection of salt to be low, generally less than 30%, or even zero; nevertheless, this external skin generally has a smaller porosity than that of the skin of the anisotropic ultrafiltration membrane.

Taking into account the thinness of the external skins, their porosity is defined by their cut-off zone, which is generally from 500 to 10,000 (molecular weight).

In practice, the external skin a) is of sufficient thickness to be obtainable free from holes, whilst at the same time it is sufficiently thin not to reduce excessively the flow rate of osmosate or hyperfiltrate. In general, the

external skins a) of the reverse osmosis membranes have thicknesses of from 0.005 to 3 $\mu$  and preferably from 0.01 to 1 $\mu$ ; those of the hyperfiltration membranes have thicknesses which can extend up to, say, 6 or even 10 $\mu$ .

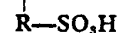
#### Anisotropic Ultrafiltration Membrane b)

The acrylonitrile polymers which constitute this anisotropic ultrafiltration membrane b) are essentially homopolymers of acrylonitrile or copolymers of this compound with at least one copolymerisable monomer. These acrylonitrile polymers generally contain at least 35% by weight of acrylonitrile radicals (or cyanoethylene units), more frequently at least 85% of such radicals. Polymers containing 35 to 85% of acrylonitrile are known under the name of "modacrylic polymers". The polymers containing at least 85% of acrylonitrile are frequently simply referred to as acrylonitrile polymers (a description used particularly in the field of textile fibres).

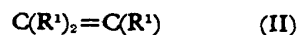
Of course, the acrylonitrile polymers can contain several comonomers, but for economic reasons it is generally not useful to employ more than 4 comonomers in addition to acrylonitrile.

The acrylonitrile comonomers can be ionic or non-ionic olefinic comonomers which contain the double bond  $>C=<$  and are copolymerisable with acrylonitrile.

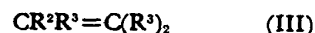
In general terms, these comonomers have the formulae



or



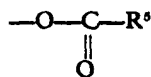
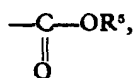
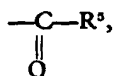
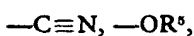
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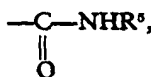
in which the various radicals  $R^1$ , which may have identical or different meanings, represent hydrogen or an alkyl radical having from 1 to 4 carbon atoms and  $R$  represents either a simple valency bond, or a divalent group, purely of hydrocarbon character, of which the free valencies are carried by a purely aliphatic (or cycloaliphatic), saturated or unsaturated, straight or branched chain group, or by an aromatic nucleus, or by a mixed chain, i.e. one containing both aliphatic and aromatic chains, such that one of the free valencies is carried by an aliphatic carbon atom and the other free valency by an aromatic carbon atom, or a  $-O-R'$  or  $-S-R'$  group, wherein  $R'$  represents a divalent group as defined above for  $R$ , or a divalent group consisting of aliphatic and/or aromatic groups, purely of hydrocarbon character, linked to one another by oxygen or

sulphur atoms, the free valencies being carried by aliphatic and/or aromatic carbon atoms, or divalent groups such as the above, of which one or more carbon atoms carry substituents such as halogen atoms or hydroxyl groups.

In the formula (III), the symbol  $R^2$ , which need not have the same meaning in various units of the formula (III), can represent a hydrogen atom, a halogen atom or an alkyl radical having from 1 to 4 carbon atoms, and the symbols  $R^3$ , which may be identical or different, can have the meaning of  $R^2$  or can each represent a group having the formula:



or



in which the symbol  $R^3$  represents a hydrogen atom or a linear or branched alkyl radical containing up to 30 carbon atoms, a cycloalkyl radical containing 5 or 6 carbon atoms in the ring, or an aryl, alkoxyaryl or aryloxyalkyl radical (preferably having at most 30 carbon atoms).

By way of illustration of the monomers of the formula (I), there may be mentioned the following (optionally salified) acids; vinylsulphonic, prop - 1 - ene - 1 - sulphonic acid, allylsulphonic acid, methallylsulphonic acid, allyloxyethylsulphonic acid, but - 1 - ene - 1 - sulphonic acid, but - 2 - ene - 1 - sulphonic acid and but - 3 - ene - 1 - sulphonic acid, hexene-sulphonic acids, especially hex - 1 - ene - 1 - sulphonic acid, methylbutenesulphonic acid, methallyloxyethylsulphonic acid, 3 - allyloxypropan - 2 - ol - 1 - sulphonic acid, allylthioethylsulphonic acid, 3 - allylthio - propan - 2 - ol - 1 - sulphonic acid, vinylbenzenesulphonic acids, especially 2 - vinyl- and 4 - vinyl - benzene - 1 - sulphonic acids, vinyloxybenzenesulphonic acids, especially 2 - vinyloxy- and 4 - vinyloxy - benzene - 1 - sulphonic acids, isopropenylbenzenesulphonic acids, especially o - isopropenylbenzene - 1 - sulphonic acid and p - isopropenylbenzene - 1 - sulphonic acid; bromovinylbenzenesulphonic acids, especially 2 - bromo- and 4 - bromo- 3 - vinyl - benzene - 1 - sulphonic acids;  $\alpha$ -methylstyrenesulphonic acid,  $\alpha$  - ethylstyrenesulphonic acid, isopropenylcumenesulphonic

acids, mono-, di- and tri - hydroxyvinylbenzenesulphonic acids, 2,5 - dichloro - 4 - vinylbenzene - 1 - sulphonic acid, isopropenyl-naphthalene - sulphonic acids, vinyl-dichloronaphthalenesulphonic acids, o- and p - allylbenzenesulphonic acids, o- and p - methallylbenzenesulphonic acids, 4 - (o- and p - isopropenylphenyl) - n - butane - 1 - sulphonic acids, vinylchlorophenylethanesulphonic acids, o- and p - allyloxybenzenesulphonic acids, o- and p - methallyloxybenzenesulphonic acids, vinylhydroxyphenylmethanesulphonic acids, vinyltrihydroxyphenylethanesulphonic acids and 2-isopropyl - ethylene - 1 - sulphonic acid.

By way of illustration of the monomers of the formula (II) or (III) which can be copolymerised with the acrylonitrile, there may be mentioned ethylene, styrene, vinyl bromide, vinyl chloride, vinylidene chloride, vinylidene cyanide, methacrylonitrile, allyl alcohol, vinyl ethers and allyl ethers, such as vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, vinyl cyclohexyl ether, vinyl benzyl ether and the corresponding allyl ethers, vinyl ketones, such as methyl vinyl ketone and ethyl vinyl ketone, unsaturated monocarboxylic acids, such as acrylic, methacrylic, crotonic and itaconic acids and their alkyl or aryl esters, in particular the methyl, ethyl, butyl and benzyl esters, cyanoacrylic and cyanomethacrylic esters, such as ethyl  $\alpha$  - cyanoacrylate, vinyl esters (which are optionally partially saponified) of linear aliphatic monocarboxylic acids, such as vinyl acetate, vinyl propionate, vinyl laurate and vinyl stearate, or of branched aliphatic monocarboxylic acids, such as the vinyl esters of acids in which the carboxyl groups is located in the  $\alpha$ -position relative to a tertiary or quaternary carbon atom, vinyl esters of aromatic acids, such as vinyl benzoate, unsaturated polycarboxylic acids, such as maleic acid or its anhydride, fumaric acid, citraconic acid, mesaconic acid and aconitic acid, as well as their monoalkyl esters, dialkyl esters and, where appropriate, trialkyl esters, alkyl being, in particular, ethyl, propyl, butyl, hexyl, 2-ethyl - hexyl, octyl or  $\beta$  - hydroxyethyl, their monocycloalkyl, dicycloalkyl and, where appropriate, tricycloalkyl esters and their monoaryl, diaryl and, where appropriate, triaryl esters, the amides of unsaturated acids, such as crotonamide, acrylamide and methacrylamide, and the reaction products of the abovementioned acids with a primary monoamine such as methylamine, ethylamine, propylamine, cyclohexylamine and aniline.

Though large amounts of these comonomers could be used, nevertheless the majority of these comonomers (above all the carboxylic compounds and sulphonic compounds) are, in practice and mainly for economic reasons, only used at the rate of at most 15% in the final copolymer. Furthermore, the comonomers used at the rate of more than 15% (in the case of copolymers containing less than 85% of

acrylonitrile) are essentially vinyl chloride and vinylidene chloride. In any case, the preferred comonomers are (optionally salified) vinyloxybenzenesulphonic acids, vinylbenzenesulphonic acids and vinylsulphonic acid, as well as methyl methacrylate; the presence of monomers containing sulphonic acid groups (which are agents which improve the dyeing affinity) is preferred.

The anisotropic ultrafiltration membranes b) obtained from the solutions of acrylonitrile polymers defined above can be planar, tubular, spiral, conical or of any other geometrical shape. They can also be in the form of hollow fibres or of coatings on solid or hollow cords.

The term "membrane having an anisotropic structure denotes a membrane which exhibits a porosity gradient from one face to the other.

More specifically, the anisotropic ultrafiltration membranes (to which paragraph b) relates) essentially consist of a macroporous substrate and a microporous skin. This microporous skin is called the "intermediate skin" in the composite membranes of the invention.

Of course there may optionally be a zone with a gradual porosity gradient between the macroporous substrate and the microporous skin.

The microporous skin of the anisotropic ultrafiltration membrane (intermediate skin) has a thickness which is generally from  $0.01\mu$  to  $5\mu$ , and for its part the macroporous substrate has a thickness generally from  $10\mu$  to 2 mm. The microporosity of the skin is such that the anisotropic ultrafiltration membrane has a cut-off zone which is from 10,000 to 300,000, corresponding to micropores of the order of 30 to 100Å. Under an electron microscope of magnification 10,000, the skin of the ultrafiltration membrane appears dense and continuous. The macroporosity of the substrate is such that the latter offers only negligible resistance to the passage of liquids through it; its macropores are largely visible under an electron microscope of magnification 10,000, their diameter generally being of the order of 0.1 to  $10\mu$ .

These anisotropic ultrafiltration membranes can be obtained by simple immersion of a liquid film of an acrylonitrile polymer solution in a coagulation bath, this liquid film preferably being supported by a suitable surface such as a plate, tube or strip of glass, metal or synthetic material. The coagulation bath is preferably a non-solvent for the acrylonitrile polymer, this non-solvent being miscible with the solvent for the said polymer; most frequently, the non-solvent consists of water or of mixtures of water and organic solvents or of aqueous solutions of electrolytes. Finally, the porosity of the anisotropic ultrafiltration membranes can be modified by a heat treatment.

It is also possible to increase the anisotropy of the said anisotropic ultrafiltration mem-

branes by effecting a partial (and relatively rapid) evaporation of the acrylonitrile polymer solution, on the side on which the microporous skin is to form, before carrying out the coagulation.

The various methods of preparation of these anisotropic ultrafiltration membranes b) is summarised since they have been known for a long time. A compilation relating to these techniques is to be found in U.S. Patents Nos. 3,615,024 and 3,567,810.

It is to be understood that the acrylonitrile polymers which can be used in the invention can contain fillers and/or plasticisers.

Equally, the membranes can consist solely of the filled or unfilled polymer film or can contain a reinforcement (constituting e.g. 10 to 70% by weight of the whole; also referred to as a screen) such as a woven fabric, knitted fabric, net or paper based on natural or synthetic fibres. If the anisotropic ultrafiltration membrane thus comprises a reinforcement it is preferable that this reinforcement should not come into direct contact with the external skin of the composite membranes of the invention.

A preferred type of reinforcement for the membranes according to the invention consists of non-woven webs of continuous filaments, also known under the name of "spunbonded" fabrics. These webs are generally obtained by extruding a fused or dissolved organic polymer through a spinneret pierced with holes, followed by an orientation of the extruded filaments, for example by stretching the bundle of filaments by means of jets of fluid (compressed air); the bundle of filaments is then collected on a moving belt, the speed and direction of which is so regulated as to form a uniform web of the desired thickness. At this stage, a calibrating process is frequently carried out or, better still, a hot calendering process which makes it possible to bond the filaments to one another, which increases the cohesion of the web. A needle-punching treatment of the web can also be carried out. A type of non-woven web preferred as the reinforcement for the purposes of the invention consists of webs such as have just been described, subjected to a treatment on both faces so as to form two external layers of relatively high specific gravity; this treatment is a heat treatment under pressure, carried out under such conditions as to produce a "flux", that is to say a softening of the filaments, which intermesh intimately with one another and form a dense and very coherent layer on each face of the web. The webs treated in this way exhibit a structure which comprises an internal layer which has retained its initial fibrous appearance, located between two smooth and glazed external layers. The use of such webs as a reinforcement (or screen) for the membranes of the invention makes it virtually impossible to disturb the permeation properties of the membrane. The manufacture

of the non-woven webs is described more generally and in greater detail on pages 179—186 of the work by J. Kovacs, Ed. Eyrolles et Masson, 1972, entitled "Les textiles non-tissés" ("The Non-Woven Textiles"). In the manufacture of the webs employed in the invention, filaments based on polyesters, especially poly(ethylene glycol terephthalate), are generally used. It is also possible to use filaments based on other polymers, such as the polyolefines (especially polypropylene, or the polyamides, polyvinyl chloride, polyvinylidene chloride, polyacrylonitrile and cellulose acetate. In general terms, satisfactory products can be obtained from elementary filaments having an average gauge of from 0.5 to 25 deniers (and preferably from 1 to 15 deniers). The non-woven webs used in the invention have a weight per m<sup>2</sup> which is generally from 10 to 250 g and preferably from 40 to 200 g.

Amongst the various configurations which the anisotropic ultrafiltration membranes can assume, there should be mentioned the cord type; in that case, the membrane is of cylindrical shape and contains, as the reinforcement, a hollow or solid cord of a textile material (see, for example, U.S. Patent No. 3,563,889 and German Patent Appln. Nos. 2,318,854, 2,332,571 and 2,339,025).

#### 30 Process for the Preparation of the Composite Membranes

The composite membranes according to the invention are advantageously prepared by a process which consists of, in a first stage, coating the skin face of an anisotropic ultrafiltration membrane of an acrylonitrile polymer, which optionally contains a reinforcement, with a solution of a polymer which is active in reverse osmosis, in an organic solvent, and then, in a second stage, evaporating this organic solvent, this evaporation (or drying) being complete or substantially complete (i.e. such that a solid skin is obtained but which nevertheless is not completely dry) when a reverse osmosis membrane is desired, whilst when a hyperfiltration membrane is desired this evaporation is only partial and is followed by a coagulation, in a non-solvent (generally water) of the polymer which is active in reverse osmosis, the said non-solvent being miscible with the solvent for the polymer which is active in reverse osmosis.

The solvent used for the process of coating with a polymer which is active in reverse osmosis is essentially a solvent in which the anisotropic ultrafiltration membrane of acrylonitrile polymer is insoluble.

It is in fact possible to select the polymer which is active in reverse osmosis from a broad and extensive range.

The coating of the anisotropic ultrafiltration membrane can be carried out by any known process.

Preferably, only the (intermediate) skin face

of the anisotropic ultrafiltration membrane is coated, but it is also possible to coat both faces (by immersing the anisotropic ultrafiltration membrane in a bath consisting of a solution of a polymer which is active in reverse osmosis), and subsequently only to dry the skin side of the anisotropic ultrafiltration membrane. In such a process, the polymer which is active in reverse osmosis, which may have been deposited on the porous substrate side (of the anisotropic ultrafiltration membrane) is generally removed simply by subsequent washing, but, whatever the case may be, the small amount of polymer, which is active in reverse osmosis, which may be fixed to this porous substrate does not have a substantial influence on the properties of the composite membrane, precisely because of the high porosity of this substrate.

However, if the process is carried out continuously, it is preferred to use the process hereafter referred to as the "dip" process, which consists of continuously passing the anisotropic ultrafiltration membrane into a bath consisting of a solution of a polymer which is active in reverse osmosis, the face of the anisotropic ultrafiltration membrane which is not to be coated being kept isolated from the bath by any suitable means. More specifically, this coating is preferably carried out by passing the anisotropic ultrafiltration membrane against (under) a drum (or roller) which is partially immersed in the bath comprising the solution of a polymer which is active in reverse osmosis; the skin face of the anisotropic ultrafiltration membrane is placed outwards, so that the porous substrate face, applied against the drum, does not come into contact with the coating bath. The Figure of Appln. No. 52270/74 (Serial Number 1,473,857) illustrates this method of working; the anisotropic ultrafiltration membrane consisting of a skin (4) and a porous substrate (3) comes up against the drum (2); the porous substrate (3) is in contact with this drum (2) whilst the skin faces outwards; whilst travelling continuously, the anisotropic ultrafiltration membrane is dipped in the bath (1) comprising the solution of a polymer which is active in reverse osmosis, and thus only the skin of this membrane is coated with the solution of this polymer which is active in reverse osmosis, so as to form a liquid film (5), which, after the subsequent treatments, will constitute the external skin of the composite membrane.

The amount per unit surface area and the concentration of the solution of a polymer which is active in reverse osmosis are in particular decided in accordance with the selected thickness of the external skin, but also in accordance with the ease of coating and of drying on the anisotropic ultrafiltration membrane. These various values of the thickness of skin, the concentration of coating solution

of salts of transition metals or of heavy metals, especially those resulting from catalytic chemical reactions or from extractions in which the solute is an organic molecule or macromolecule, such as sugar solutions, solutions containing enzymes, proteins, nucleic acids and other thermolabile products; solutions which contain both salts and organic molecules, such as foodstuff juices, sugary liquors, fruit juices, milk, meat juices and whey; biological liquids, especially those containing urea, such as blood plasma, dialysis baths used in haemodialysis, and ultrafiltrates resulting from the ultrafiltration of blood; all these solutions can furthermore contain insoluble constituents in suspension.

The membranes according to the invention exhibit numerous advantages, especially by the virtue of their simplicity and their good performance characteristics; furthermore, these membranes are economical to prepare, in view of the fact that they are based on quite common polymers such as acrylonitrile copolymers.

#### EXAMPLES

The following Examples further illustrate the present invention.

##### Example 1

A composite membrane is prepared on a non-woven screen. This screen consists of a non-woven web of continuous (spun-bonded) filaments of poly(ethylene glycol terephthalate) (Registered Trade Mark Bidim); the filaments have a mean gauge of 2 deniers; the web weighs 70 g per square metre; the two surfaces have a smooth and glazed appearance obtained by calendaring between two rollers at 240°C, which apply to the web a force of 60 tonnes over a length of 1.40 m.

A solution having the following composition is cast, at a thickness of 50 $\mu$ , onto this screen: 4 g of water, 76.45 g of dimethylformamide, 0.2 g of LiCl, 19.3 g of an acrylonitrile/methyl methacrylate/sodium methallylsulphonate terpolymer, these monomers being present in the respective proportions by weight of 91.4/7.75/0.85.

After 60 seconds evaporation in air, coagulation is carried out by immersion in pure water at 25°C. Finally, a treatment in water at 60°C is carried out for 15 minutes.

This screen-reinforced anisotropic ultrafiltration membrane b) exhibits a throughput of pure water, under 2 bars, of 4000 l/day.m<sup>2</sup>. It contains 15 g of acrylonitrile copolymer per square metre. Its degree of rejection of lysozyme (molecular weight 15,000) is 100%.

This anisotropic ultrafiltration membrane is dried for 1 minute at 50°C (residual moisture content: 30% by weight of the dry membrane). Fine droplets of a solution containing 0.125% by weight, in methoxyethanol, of a sulphonated (acid) polysulphone as described

in examples of U.S. Patent 3,709,841, but having an ion exchange capacity of 0.935 milliequivalent/g, are sprayed (onto this membrane) by means of an electrostatic spray gun for 30 seconds (at a rate of 0.3 l/hour). The membrane is dried for one minute at 60°C, is again sprayed for 30 seconds and is again dried for one minute at 60°C, and the whole is immersed in water.

This membrane is used in a reverse osmosis operation for treating a 5 g/l aqueous solution of NaCl under a differential pressure (that is to say a difference in pressure between the two sides of the membrane) of 30 bars.

A flow rate of permeate of 400 l/day.m<sup>2</sup> is observed, with a degree of rejection of salt of 91%. The external skin a) has a thickness of about 0.35 $\mu$ .

##### Example 2

Example 1 is repeated, but replacing the methoxyethanol by a mixture of methoxyethanol and dioxane in the respective proportions by weight of 90/10.

A membrane which gives a flow rate of permeate of 600 l/day.m<sup>2</sup> and a degree of rejection of 94.5% (the measurements being carried out under the conditions of Example 1) is obtained. The external skin a) has a thickness of about 0.3 $\mu$ .

##### Example 3

Example 1 is repeated, but replacing the methoxyethanol by a mixture of methoxyethanol, dioxane and water in the respective proportions by weight of 19.8/79.2/1.

A membrane which gives a flow rate of permeate of 1200 l/day.m<sup>2</sup> and a degree of rejection of 85% (the measurements being carried out under the conditions of Example 1) is obtained. The external skin a) has a thickness of about 0.25 $\mu$ .

It will be appreciated that acrylonitrile polymers are referred to in Application No. 52270/74 (Serial No. 1,473,857) as being suitable constituents in the preparation of the complex polyelectrolytes which may form the anisotropic ultrafiltration membrane of the composite membranes claimed in Application No. 52270/74. Naturally, it is not intended that the acrylonitrile polymers used in the present invention should be in the form of complex polyelectrolytes and, for the avoidance of doubt, no claim is made herein to the essential acrylonitrile polymer of the anisotropic ultrafiltration membranes being in the form of a complex polyelectrolyte.

Subject to this disclaimer:

#### WHAT WE CLAIM IS:—

1. A semi-permeable composite membrane which comprises applied to one another, a) an outer skin consisting of a polymer which is water-insoluble, is active (as hereinbefore defined) in reverse osmosis and has a

sufficiently high molecular weight for the anisotropic ultrafiltration membrane b) to have a degree of rejection of 100% with respect to solutions of this polymer, and

- 5 b) an anisotropic ultrafiltration membrane of an acrylonitrile polymer, the outer skin a) being in contact with at least the less porous side of the anisotropic ultrafiltration membrane b).

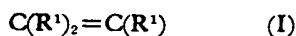
10 2. A membrane according to Claim 1, in which the outer skin a) has a total thickness not exceeding  $3\mu$ .

3. A membrane according to Claim 2, in which the outer skin a) has a total thickness not exceeding  $1\mu$ .

15 4. A membrane according to Claim 1 which is particularly suitable for use in reverse osmosis and the outer skin is dense.

5. A membrane according to Claim 1, which is particularly suitable for use in hyperfiltration and the outer skin has a cut-off zone of from 500 to 10,000.

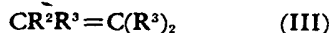
20 6. A membrane according to any one of Claims 1 to 5, in which the acrylonitrile polymer contains at least 35% of acrylonitrile radicals and comonomer or comonomers having the formula:



or

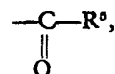


or

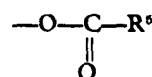
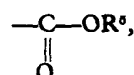


in which each of the  $R^1$  radicals, which may have identical or different meanings, represent hydrogen or an alkyl radical having from 1 to 4 carbon atoms, R represents either a valency bond, or a divalent group, purely of hydrocarbon character, of which the free valencies are carried by a purely aliphatic (or cycloaliphatic), saturated or unsaturated, straight or branched chain group, or by an aromatic nucleus, or by a mixed chain (as hereinbefore defined) such that one of the free valencies is carried by an aliphatic carbon atom and the other free valency by an aromatic carbon atom, or a  $-O-R'$  or  $-S-R'$  group, wherein  $R'$  represents a divalent group as defined under R, or a divalent group consisting of aliphatic and/or aromatic groups, purely of hydrocarbon character, linked to one another by oxygen or sulphur atoms, the free valencies being carried by aliphatic and/or aromatic carbon atoms, or a said divalent group, one or more carbon atoms of which are substituted by halogen atoms and/or hydroxyl groups, each  $R^2$  radical, which may have identical or different meanings in various units of formula (III), represents a hydrogen atom, a halogen atom or an

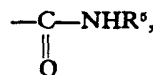
alkyl radical having from 1 to 4 carbon atoms, and each  $R^3$  radical, which may have identical or different meanings, is as defined under  $R^2$  or represents a group of the formula:



65



or



in which  $R^5$  represents a hydrogen atom or a linear or branched alkyl radical containing up to 30 carbon atoms, a cycloalkyl radical containing 5 or 6 carbon atoms in the ring, or an aryl, alkoxyaryl or aryloxyalkyl radical.

7. A membrane according to Claim 6, in which the comonomer is an optionally salified vinyloxybenzenesulphonic acid, vinylbenzenesulphonic acid or vinylsulphonic acid, or methyl methacrylate.

8. A membrane according to any one of Claims 1 to 7, in which the polymer which is active in reverse osmosis is a polymer with sulphonic acid groups or a polymer with quaternary ammonium groups.

9. A membrane according to Claim 8, in which the polymer which is active in reverse osmosis is a sulphonated polyaryl ether sulphone.

10. A membrane according to any one of Claims 1 to 9, which is reinforced.

11. A membrane according to Claim 10 which is reinforced by a woven fabric, knitted fabric or net.

12. A membrane according to Claim 10 or 11, in which the reinforcement is a non-woven web of continuous filaments, which has been smoothed and glazed at the surface by a heat treatment under pressure.

13. A membrane according to Claim 1 substantially as hereinbefore described.

14. Process for the preparation of a membrane as claimed in any one of the preceding Claims which comprises coating the skin face of an anisotropic ultrafiltration membrane of an acrylonitrile polymer, optionally containing a reinforcement, with a solution of a polymer, which is active in reverse osmosis, in an organic solvent, and evaporating the organic solvent.

15. Process according to Claim 14 for the preparation of a reverse osmosis membrane in

which the evaporation is complete or substantially complete.

5 16. Process according to Claim 14 for the preparation of a hyperfiltration membrane in which the evaporation is partial and the membrane is then coagulated in a non-solvent for the polymer which is active in reverse osmosis.

17. Process according to Claim 14 substantially as hereinbefore described.

18. Process according to Claim 14 substantially as described in any one of the Examples. 10

19. A composite membrane as defined in Claim 1 whenever prepared by a process as claimed in any one of Claims 14 to 18.

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